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Compact, Inexpensive, Safe, and Rapidly Refuelable Hydrogen Storage in Cryogenic Pressure Vessels

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Abstract

Hydrogen storage is often cited as the greatest obstacle to achieving a hydrogen economy free of environmental pollution and dependence on foreign oil. A compact high-pressure cryogenic storage system has promising features to the storage challenge associated with hydrogen-powered vehicles. Cryogenic pressure vessels consist of an inner vessel designed for high pressure (350 bar) insulated with reflective sheets of metalized plastic and enclosed within an outer metallic vacuum jacket. When filled with pressurized liquid hydrogen, cryogenic pressure vessels become the most compact form of hydrogen storage available. A recent prototype is the only automotive hydrogen vessel meeting both Department of Energy's 2017 weight and volume targets. When installed onboard an experimental vehicle, a cryogenic pressure vessel demonstrated the longest driving distance with a single H₂ tank (1050 km). In a subsequent experiment, the vessel demonstrated unprecedented thermal endurance: 8 days parking with no evaporative losses, extending to a month if the vehicle is driven as little as 8 km per day. Calculations indicate that cryogenic vessels offer compelling safety advantages and the lowest total ownership cost of hydrogen storage technologies. Long-term (~10 years) vacuum stability (necessary for high performance thermal insulation) is the key outstanding technical challenge. Testing continues to establish technical feasibility and safety.

Introduction

Unlike other fuels, hydrogen (H₂) can be generated and consumed without producing carbon dioxide (CO₂). This creates both significant engineering challenges and unsurpassed ecological advantages for H₂ as a fuel, while enabling an inexhaustible (closed) global fuel cycle based on the cleanest, most abundant, natural, and elementary substances: H₂, O₂, and H₂O. If generated using light, heat, and/or electrical energy from solar, wind, or (future) fusion power sources, H₂ becomes a versatile, storable, and universal carbonless energy carrier, a necessary element for future global energy system(s) aimed at being free of air and water pollution, CO₂, and other greenhouse gases [1].

The predominant technical barrier limiting widespread use of H₂ automobiles is storing enough hydrogen fuel onboard to achieve sufficient (500+ kilometers) driving range in a compact, lightweight, rapidly refuelable, and cost-effective system. There are three major conceptual approaches to storing hydrogen onboard automobiles, and they all face fundamental limits:

1. Low pressure liquid hydrogen (LH₂) storage systems have high density and reasonably low cost [2], but they suffer from evaporative losses after a short period of inactivity (1-3 days) that can leave the driver stranded without fuel if the vehicle remains parked for a long time (~2 weeks).
2. Compressed gaseous hydrogen (CGH₂) storage systems are bulky and difficult to package within a vehicle. The large storage vessels necessary for 500 km range are expensive due to the amount of strong materials (composite, metal) necessary [3][4].
3. Storage systems based on metal hydrides or sorbent structures demand careful thermal management for refueling and H₂ supply. Thermal management equipment increases system complexity, cost, weight, and volume, and is still insufficient for practical refueling times [5].

Cryogenic Pressure Vessels

Over the last decade we have developed an approach that combines existing storage technologies (cryogenic and high-pressure) to capture the advantages of both: *cryogenic* pressure vessels. For pressure vessels of a given size and cost, cryogenic vessels store substantially more hydrogen than ambient temperature vessels without the additional weight and cost of hydrogen absorbent materials but with far greater thermal endurance than conventional (i.e. low pressure) cryogenic LH₂ tanks. Cryogenic pressure vessels can essentially eliminate evaporative losses for practical automotive operation scenarios.

Cryogenic pressure vessels comprise a high-pressure inner vessel made of carbon-fiber-coated metal (similar to those used for storage of compressed gas), a vacuum space filled with numerous sheets of highly reflective metalized plastic (for high performance thermal insulation), and a metallic outer jacket (Figure 1). Cryogenic pressure vessels operate at low temperature (down to 20 K) and are designed for high pressure (350 bar), typically storing H₂ at considerably higher density than CGH₂, and possibly even higher density than LH₂.

As a direct consequence of storing high density H₂, cryogenic pressure vessels are compact and cost effective, reducing cost by reducing the amount of expensive materials (composite and metal) necessary for manufacture. Cryogenic pressure vessels are therefore predicted to be less expensive than competitive technologies (Figure 2) at the small capacities necessary for efficient compact vehicles (5.6 kg H₂, energetically equivalent to 5.6 gallons of gasoline). Even greater cost advantages exist for larger capacities (10.4 kg) necessary for large vehicles or longer driving range.

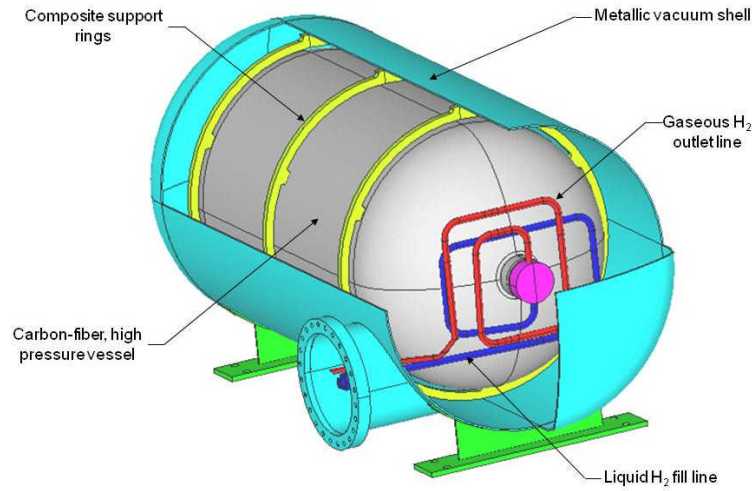


Figure 1. Generation 2 cryogenic pressure vessel. The inner vessel is an aluminum-lined, carbon fiber-wrapped (Type 3) pressure vessel similar to those typically used for storage of compressed gases. This vessel is surrounded by a vacuum space filled with numerous sheets of highly reflective metalized plastic (minimizing heat transfer into vessel), and an outer metallic jacket. The outer jacket measures 120 cm (47 in) long and 58.5 cm (23 in) outer diameter, and stores 151 liters of H_2 . The vessel outer volume is 298 liters, while the system weight and volume (including all accessories) are 187 kg and 323 liters, respectively.

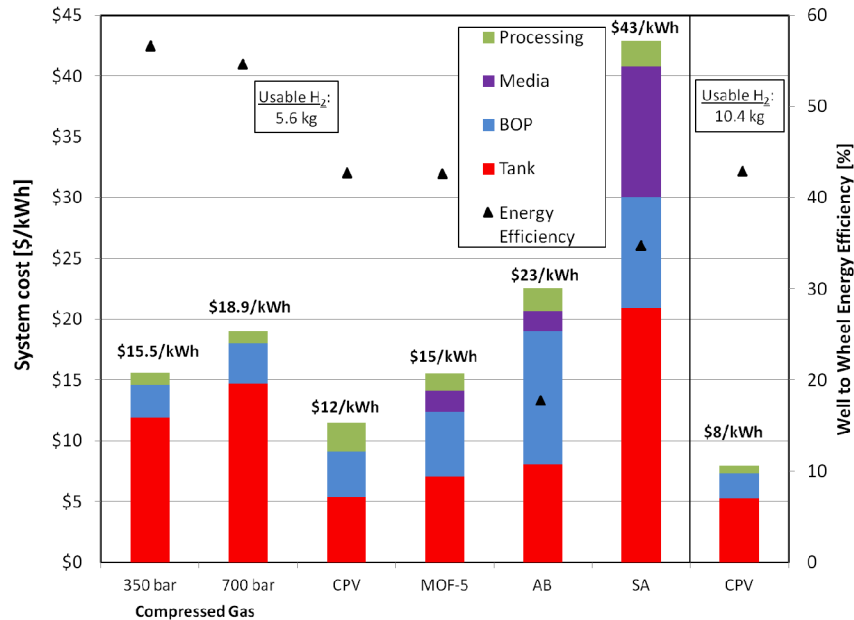


Figure 2. Estimated large-scale (500,000 units manufactured per year) cost for storing 5.6 kg of usable H_2 with different storage technologies, and cost of storing 10.4 kg H_2 in a cryogenic pressure vessel (right). The figure also shows well to wheel efficiency (triangles) in the right scale. First two bars at the left (350 and 700 bar) are for compressed H_2 , while CPV, MOF-5, AB and SA respectively stand for Cryogenic Pressure Vessels, Metallic Organic Framework, Ammonia Borane, and Sodium Alanate [6], [7], [8], [9], [10], [11].

Dormancy and Evaporative Losses

Cryogenic pressure vessels largely solve the problems typically associated with LH₂ tanks: evaporative losses after a short period of inactivity, evaporative losses for short daily driving distances, and danger of being stranded due to fuel evaporation. Favorable thermodynamics eliminate evaporative losses in cryogenic pressure vessels because the higher design pressure (350 bar vs. 6 bar for conventional LH₂ tanks) enables hydrogen containment even as the vessel warms up and pressurizes.

The dormancy (period of inactivity before a vessel releases H₂ to reduce pressure build up) is an important parameter for cryogenic storage acceptability. Dormancy can be calculated from the first law of thermodynamics and the properties of H₂ [12], and can be illustrated with a diagram of H₂ thermodynamic properties (Figure 3) to simplify visualization and graphical calculation of H₂ vessel dormancy.

Figure 3 uses axes of internal energy and density instead of more traditional temperature and pressure. Dormancy calculations begin by identifying the initial thermodynamic state in Figure 3 of the H₂ contained in the vessel. From this initial point (e.g., Point 1), the thermodynamic state of H₂ fuel onboard a parked vehicle moves horizontally to the right (warming at constant density) as heat enters from the environment, until H₂ pressure reaches the vessel maximum and some H₂ needs to be used or vented. The cumulative thermal energy absorbed while a car is parked can be calculated by multiplying the amount of H₂ in the vessel by the total change in its specific internal energy. This total thermal energy is shown as the *area* in Figure 3 under the horizontal line joining the initial and final points in the process (neglecting temperature stratification and vessel thermal capacity). Dormancy is then equal to the total heat absorbed (the area under the line) divided by the environmental heat transfer rate.

An appropriate choice of scales in Figure 3 radically simplifies dormancy calculations. The grid scale in the internal energy (horizontal) axis is set at 86.4 kJ/kg H₂, which converts to 1 Watt-day/kg H₂ (1 day=86,400 seconds). The grid scale in the vertical axis represents 1 kg H₂. Therefore, the area of a grid square represents 1 Watt-day of heating. The total change in internal energy (in Watt-days) can be easily calculated by counting the squares under the horizontal line representing the parking process. Dormancy (days) is calculated by dividing the internal energy change (in Watt-days) by the rate of heat transfer (in Watts).

As an illustration consider a parked automobile with a low pressure LH₂ tank with 140-liter internal volume and 6 bar maximum working pressure, which is 80% full with 8 kg LH₂ at 20 K and 1 bar (Point 1 in Figure 3). Once the vehicle is parked heat transfer warms the H₂ increasing both its temperature and pressure. Dormancy ends in this case when the pressure reaches 6 bar (Point 2), when venting H₂ or driving vehicle becomes necessary to maintain pressure within the vessel rating. Total heat absorbed during this process from Point 1 to Point 2 can be calculated by counting the number of squares (8 Watt-days) in the area marked in green. Dormancy can then be calculated by dividing 8 Watt-days by the heat transfer rate (e.g. 2 days for a vessel absorbing heat at a rate of 4 Watts).

In contrast, an auto equipped with a cryogenic pressure vessel initially filled with 8 kg LH₂ at 1 bar and 20 K can remain parked until the pressure reaches 350 bar (Point 3 in the figure) without venting any H₂. Counting squares under the line joining Point 1 and Point 3 (green and red areas) we obtain 8+48=56 Watt-days, *seven times* greater thermal endurance than a conventional LH₂ tank.

Figure 3 thus illustrates the dramatic dormancy advantage of automobiles with cryogenic pressure vessels over those with low-pressure LH₂ vessels.

Furthermore, unlike conventional LH₂ vessels, cryogenic pressure vessels dramatically extend dormancy as the vehicle is driven. For example, if the parked vehicle is driven when the H₂ is at state 3 (Figure 3), consuming 2 kg of H₂ fuel, the remaining H₂ in the vessel expands and cools following a constant entropy line from Point 3 to Point 4, extending the vessel thermal endurance by an additional 48 Watt-days before any losses occur (at Point 5). Further driving substantially extends dormancy, essentially eliminating fuel evaporation for even very moderate driving patterns.

In principle, Figure 3 enables simple analyses of arbitrary cycles of driving and parking periods. Evaporative losses and dormancy are easily calculable given a driving schedule, vessel volume, and thermal performance (i.e. heat transfer leak rate).

It should be noted that figure 3 is somewhat conservative because it neglects secondary effects such as vessel thermal capacity and heat potentially absorbed by conversion between the two states of nuclear spin arrangement (i.e., *para*-H₂ conversion to *ortho*-H₂) of H₂ molecules. Both of these effects tend to increase the dormancy of the vessels, but are most significant only for warmer temperatures ($T > 77$ K). Both effects are negligible at the very low (i.e. 20-30 K) temperatures where low pressure LH₂ tanks operate [13].

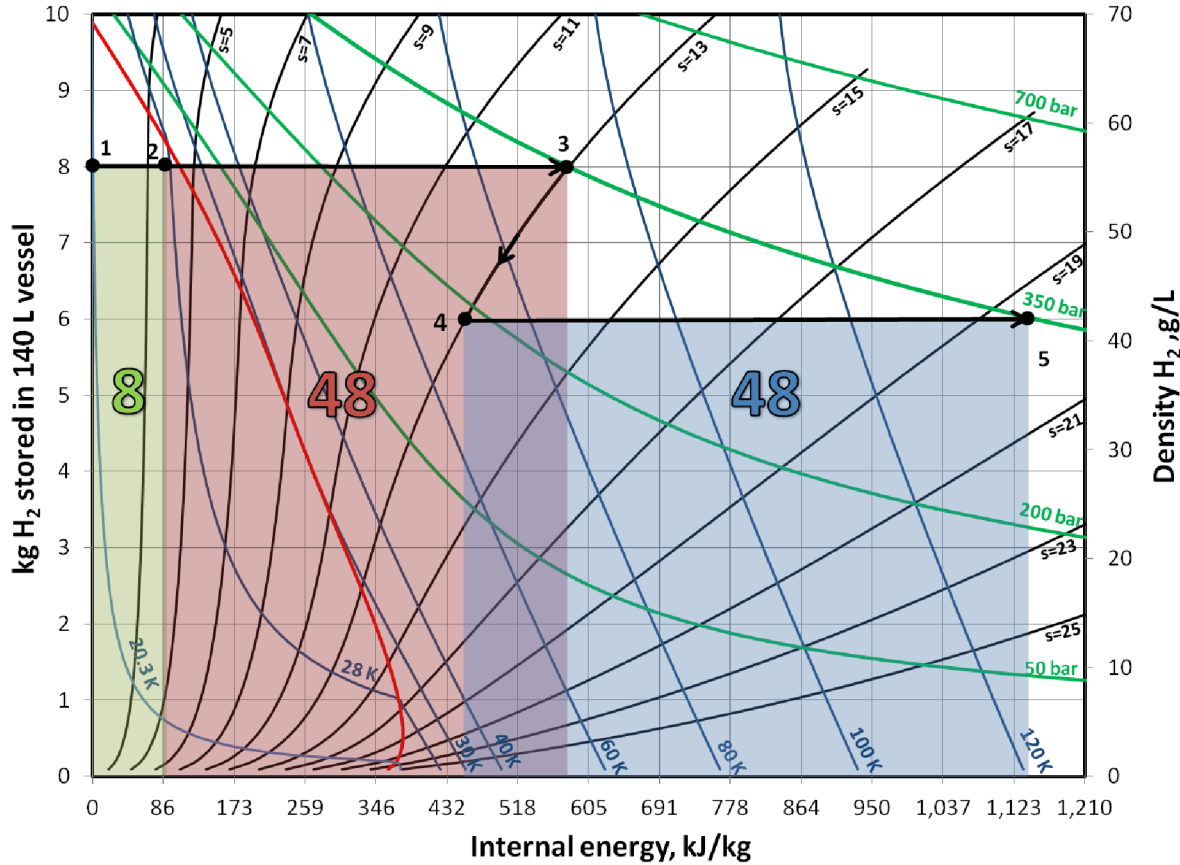


Figure 3. Phase diagram for H₂ showing density (right vertical axis) and internal energy (horizontal axis), with lines for constant pressure (green), temperature (blue) and entropy (black). The figure also shows a red saturation line that separates the single phase region (right) from the two-phase liquid-vapor region (left). A second vertical axis in the left shows the mass of H₂ contained in a vessel with 140 L internal volume, which would store 10 kg of LH₂ at 20 K and 1 bar. The figure also shows points and areas representing dormancy (in Watt-days) of conventional LH₂ tanks (green area) and cryogenic pressure vessels (green+red+blue areas).

Cryogenic pressure vessels' reduced sensitivity to environmental heat transfer was demonstrated in a recent experiment (Figure 4). The experiment started by filling the cryogenic vessel 96% full (10.2 kg) of saturated LH₂ at 2 bar. From this point, the vessel contained the hydrogen with no evaporative losses for 8.5 days with ~4.5 Watt heat transfer rate.

Extracting 1 kg H₂ after the long dormancy experiment (day 9 in Figure 4) isentropically depressurized the cryogenic vessel to 205 bar. Subsequent pressurization (days 9-19) is visibly slower than the initial pressurization (days 1-8). The reason for the slower pressurization was identified as para-ortho H₂ conversion [13].

Hydrogen has two states of nuclear spin orientation: para-H₂ and ortho-H₂. Para-H₂ is the low energy form stable at LH₂ temperature (20 K). As H₂ heats up from 20 K, equilibrium shifts toward ortho-H₂, reaching the so-called normal composition (25% para and 75% ortho) at room temperature. Liquid hydrogen (typically delivered as para-H₂ for stability) will therefore convert to ortho-H₂ as it warms up, absorbing considerable thermal energy (700 kJ/kg – for comparison,

the heat of vaporization is 452 kJ/kg) in the process [14]. Para-ortho H_2 conversion is synergistic with long-term H_2 storage in cryogenic pressure vessels, because energy absorption (blue area in Figure 4) extends dormancy (by ~ 1 week in Figure 4). Conversion kinetics have been shown to be of the same order of magnitude of typical parking durations (days to weeks) [15], [16].

After extracting H_2 from the vessel a few more times, we completed a month's experiment while still retaining 7.7 kg H_2 in the vessel. Extracting 2.5 kg H_2 was therefore sufficient to avoid evaporative losses for 1 month. Considering an energy efficient vehicle with 100 km/kg H_2 fuel economy, driving as little as 250 km per month (8 km/day) would be sufficient to avoid evaporative losses.

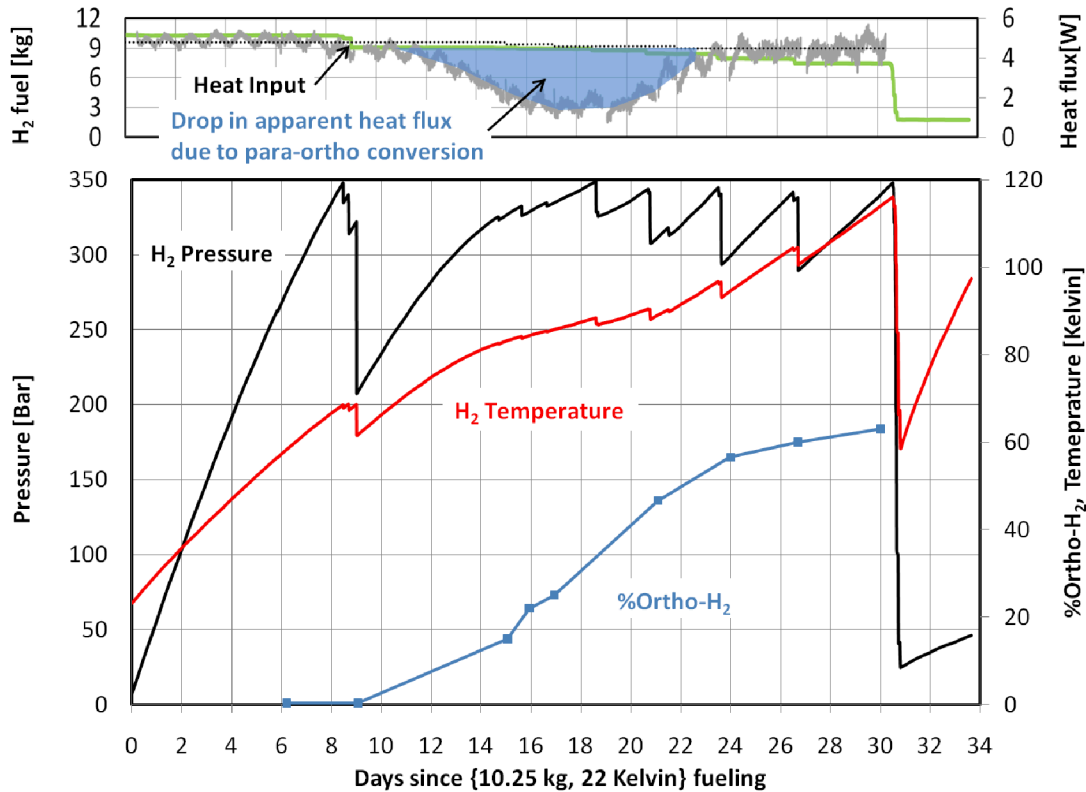


Figure 4. Results from month-long dormancy experiment. The figure shows pressure (black line, left scale), temperature (red line, right scale), ortho concentration (blue line, right scale), hydrogen mass (green line, left scale, upper chart), and apparent heat transfer (gray line, right scale, upper chart).

Cryogenic Vessel Testing

Cryogenic pressure vessels rely on aluminum-lined, fiber-wrapped vessels typically used for storing compressed gas (Figure 1). These vessels are not designed for cryogenic operation, and from the very beginning we have considered the risk of vessel failure due to large stresses caused by differential contraction of aluminum and composite. We therefore have conducted extensive testing by cycling several vessels to cryogenic temperature and back to ambient temperature one hundred times. While preliminary, the results have indicated satisfactory performance, especially when the vessel is cold filled at high pressure. The largest thermal

stresses occur during low pressure cold fills, and further study is necessary to determine cycle life at these conditions [17].

Aside from cycle testing, we have conducted a variety of additional tests following procedures specified by the U.S. Department of Transportation (DOT) [18], the Society of Automotive Engineers (SAE) [19], and the International Organization for Standardization (ISO). Tests included pressure cycle and burst, environmental, drop from 3 m, drop from 10 m, gunfire, bonfire, and cryogenic cycle and burst [20][21]. In every case, the vessels met the test criteria.

Technology Validation

After completing all certification tests we had enough confidence in the technology to install a cryogenic pressure vessel onboard a hydrogen-fueled experimental vehicle. The first cryogenic vessel installed on a vehicle (generation 1 prototype) operated at a maximum pressure of 245 bar with a 135 L internal volume and 9.3 kg LH₂ capacity. The vessel was installed onboard a Ford Ranger pickup truck powered by a hydrogen internal combustion engine [22]. The Ford Ranger underwent initial shakedown testing at LLNL and demonstrated refueling and operation on both liquid and compressed hydrogen validating operation on both at SunLine Transit (Thousand Palms, California).

Following this proof of concept, an improved generation 2 prototype vessel (Figure 1) was developed. The generation 2 cryogenic pressure vessel is stronger (340 bar) with a greater internal volume (151 L) storing more fuel (10.4 kg LH₂) than the previous vessel in a total package that is considerably more compact [8]. The generation 2 vessel was compact and light enough to meet the Department of Energy's 2010 targets for weight and volume (Figure 5). After satisfactory pressure, cryogenic and vacuum testing, the vessel was installed in an experimental hydrogen hybrid vehicle (Figure 6).

The hydrogen hybrid vehicle was then test driven 1050 km on a single tank fill of LH₂ – the longest for a hydrogen vehicle [8]. The drive was conducted on-site at LLNL so traffic and speeds were atypical. Under typical driving we would expect 800 km driving range based on the vehicle's EPA fuel economy rating (80 km/kg H₂) and the capacity of the storage tank.

We subsequently designed and built an improved vessel (generation 3) that takes advantage of the large thermal endurance of cryogenic pressure vessels (Figure 3) by reducing thermal insulation thickness (1.5 cm vs. 3 cm in generation 2). The generation 3 vessel stores the same amount of hydrogen (10.4 kg) as the generation 2 vessel within a package that is 23% more compact (225 L vs. 297 L outer vessel volume) [8]. Compact construction makes the generation 3 prototype the first vessel to meet the DOE 2017 weight and volume targets (Figure 5).

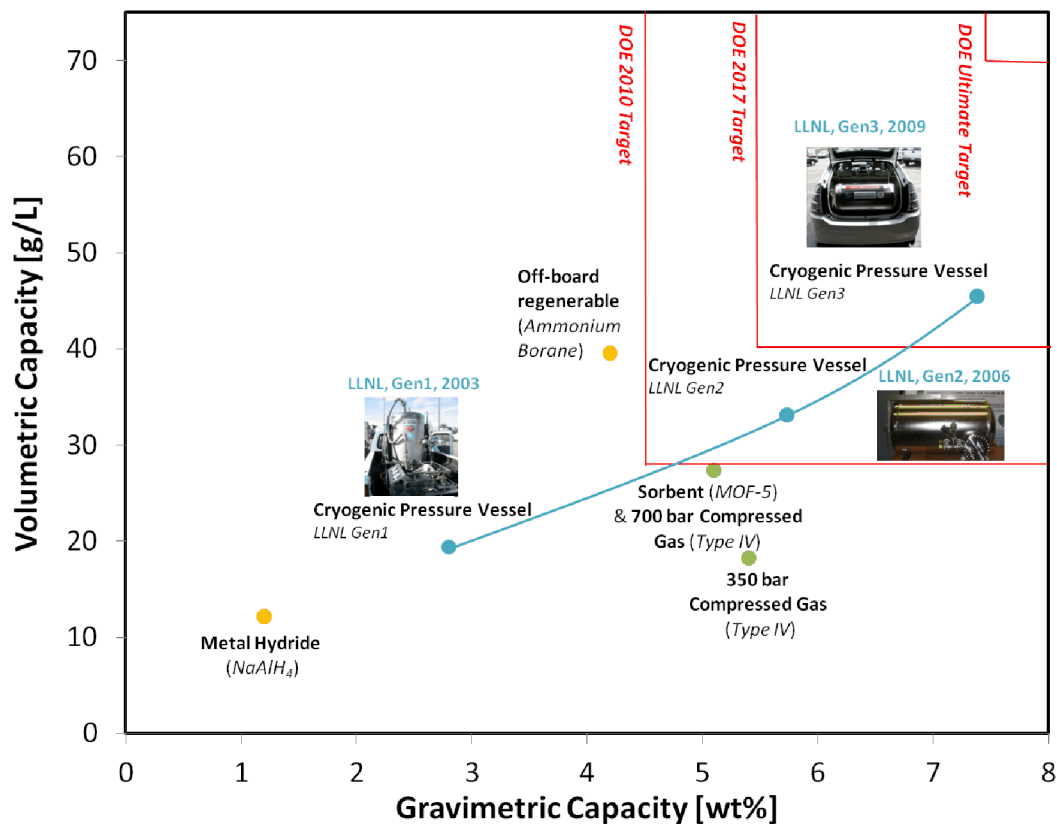


Figure 5. Gravimetric and volumetric energy storage density for different hydrogen storage technologies [6] and cryogenic pressure vessel prototypes (generations 1, 2 and 3) vs. Department of Energy (DOE) 2010, 2017 and ultimate weight and volume targets.



Figure 6. Generation 2 cryogenic pressure vessel installed onboard a hydrogen-fueled Toyota Prius experimental vehicle.

Safety

Cryogenic pressure vessels offer a number of potential safety advantages over compressed gas vessels. The most dramatic and perhaps counterintuitive is the radically lower theoretical burst energy of low temperature H₂. Figure 7 shows the theoretical maximum mechanical energy released by a sudden adiabatic expansion to atmospheric pressure (e.g. in a vessel rupture) of high-pressure hydrogen gas from three temperatures (60 K, 150 K and 300 K). Normal H₂ stored at 100 bar and 300 K will release a maximum mechanical energy of 0.57 kWh/kg H₂ if suddenly (i.e. adiabatically) expanded to atmospheric pressure, cooling substantially in the process. Counterintuitively, this maximum energy release increases only slightly with much higher H₂ pressures. Raising vessel pressure to 1000 bar (1000% increase from 100 bar) increases maximum mechanical energy release by less than 10%. This is because higher pressure leads to faster cooling, making expansion volume a decreasing function of pressure (i.e. high pressure H₂ expands *less* than low pressure H₂). Expansion energy (calculated as the integral of $p dv$ [23]) is therefore quasi-insensitive to pressure for $p > 100$ bar because the smaller expansion volume compensates for the higher pressure.

In sharp contrast, *temperature* has a very strong influence on the theoretical maximum mechanical energy. Cooling hydrogen gas from 300 to 150 K and especially to 60 K dramatically reduces expansion volume and mechanical energy (that is actually a linear function for ideal gas [23]), reducing the potential damage of a sudden rupture. The low burst energy and high hydrogen storage density of cryogenic temperatures combine synergistically, permitting smaller vessels which can be better packaged onboard to withstand automobile collisions.

The vacuum jacket surrounding the cryogenic pressure vessel (Figure 1) also contributes to safe operation by offering a second layer of protection, eliminating environmental impacts over the life of the pressure vessel. The vacuum jacket also provides expansion volume to mitigate shocks from hydrogen release. In the most likely failure scenarios (rupture of the fill/outlet tubes or bullet impact during certification testing), hydrogen escapes the inner high-pressure vessel through a small hole (a few mm diameter). Instead of this high pressure, high energy jet directly flowing into the environment, it first expands into the vacuum space. The vacuum jacket subsequently vents into the environment as its relief device (rupture disc) opens. Considering that rupture discs are typically larger than pressure vessel orifices, H₂ release from the vacuum jacket will occur at a much-reduced pressure. We have calculated that cryogenic operation and vacuum jacketing reduces expansion thrust by a factor of 10 and power by a factor of 30 with respect to a compressed gas tank at ambient temperature [24]. Mitigation of the dissipation power by expansion into vacuum space combined with the lower energy of cold hydrogen may therefore lead to very safe systems that cause little damage even after sudden failure. Further research is necessary to fully analyze the safety implications of these results.

Cryogenic vessels also avoid the fast fill heating and overpressures (up to 25%) typical of compressed H₂ vessels, consequently operating at higher safety factors, especially as driving the automobile cools the remaining hydrogen fuel and reduces average hydrogen pressures further over typical driving and refueling cycles. Finally, due to the high storage density of cryogenic hydrogen and the relatively low refueling pressure, the number and amplitude of pressure peaks in a cryogenic pressure vessel can be lower than in ambient high-pressure vessels.

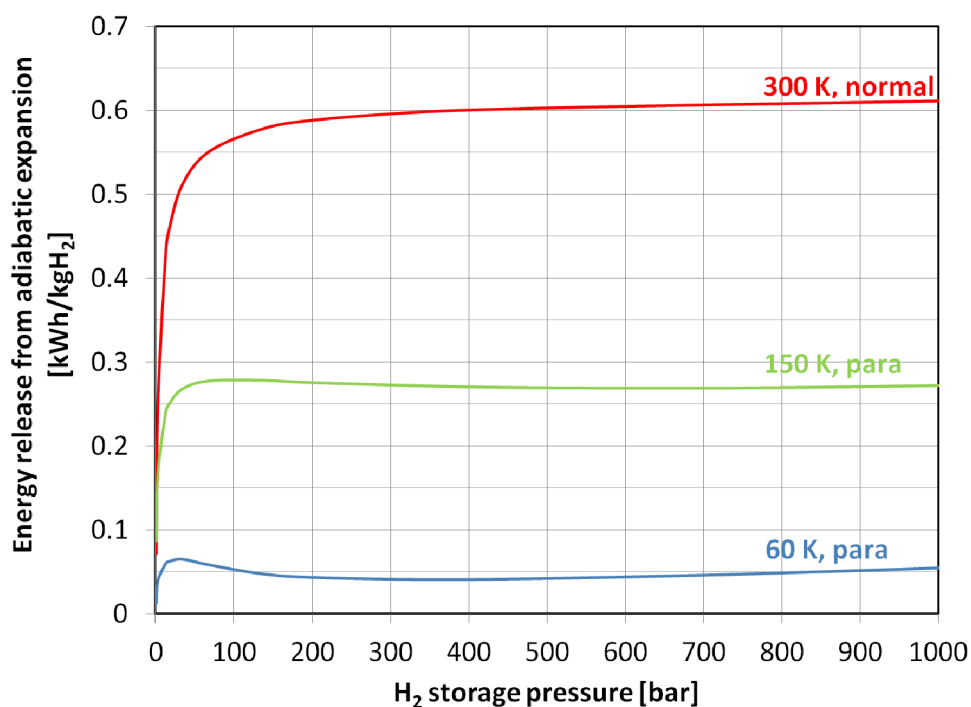


Figure 7. Maximum mechanical energy (per kilogram of H₂) released upon instantaneous expansion of H₂ gas (e.g. from a pressure vessel) as a function of initial storage pressure at 60 K, 150 K, and 300 K. For comparison, note that the lower heating value of hydrogen is 33.3 kWh/kg. The figure reports normal-H₂ expansion energy at 300 K and para-H₂ expansion energy at 60 K and 150 K. In the latter two cases the real adiabatic expansion energies are slightly lower because the para-H₂ content is less than 100% before expansion (between 99.8% and equilibrium, depending on the previous use of the storage and the actual ortho-to-para H₂ transition rate).

Refueling

Cryogenic vessel temperature and pressure are strong functions of use patterns. After a cryogenic hydrogen fill, pressure vessels will remain cold and unpressurized if frequently driven due to (nearly) isentropic H₂ expansion during gas extraction, thereby enabling efficient refueling from conventional low pressure (~6 bar) LH₂ Dewars. Extended periods of parking, however, will warm up and pressurize the vessel due to heat transfer from the environment. Refueling warm vessels with low pressure LH₂ is slow and inefficient, resulting in high evaporative losses. A better solution is needed for practical cryogenic pressure vessel refueling.

Liquid hydrogen pressurization appears a viable solution. A pump may take LH₂ from a low pressure Dewar and deliver it at 30-60 K and 200-875 bar, enabling direct dispensing into even warm and/or pressurized vessels while minimizing evaporative losses.

High efficiency LH₂ pumps are now commercially available. Manufactured by Linde, a leading supplier of cryogenic equipment, the LH₂ pump satisfies the requirements for rapid cryogenic pressure vessel refueling [25]. Aside from providing rapid refueling rates (100 kg/hr) and low evaporative rates (<3%), the pump takes advantage of the inherently large compressibility of LH₂ to deliver high density H₂ (80 kg/m³ at 300 bar and potential for 90 kg/m³ at 875 bar) [26]. Moreover, evaporated hydrogen is not vented. Instead, it is recirculated into the station LH₂ Dewar, helping maintain pressurization.

A potential issue with direct dispensing from a LH₂ pump is the variability in the amount of hydrogen in a “full” tank as a function of initial conditions. While a cold tank can be filled to full capacity, a warm vessel can only be refueled to lower capacity to avoid evaporative losses when thermal equilibrium between the hydrogen and the vessel is reached [26]. Fill variability may be acceptable to consumers because it is self-regulating: an infrequently driven vehicle is filled partially, but also requires less fuel because it is typically unused. A frequently driven vehicle has a cold vessel that can be filled to capacity, enabling long driving range.

Liquefaction Cost and Energy

One of the most frequently raised issues with respect to cryogenic pressure vessel operation is H₂ liquefaction. Liquefaction is expensive (\$1.61/kg H₂ [11]) and energetically intensive (13.14 kWh/kg vs. 3.2 kWh/kg for compression to 700 bar [27]), resulting in a low well to wheels efficiency (Figure 2). LH₂ is therefore frequently considered impractical for large-scale transportation. However, LH₂ has virtues that overcome liquefaction cost and energy issues. Addressing first the issue of cost, we notice two important facts:

- LH₂ delivery is considerably less expensive than compressed H₂ delivery: a LH₂ tanker truck has the capacity of 7 tube trailers typically used for compressed H₂ delivery (4,000 kg H₂ vs. 550 kg H₂ [11]), minimizing labor and truck capital cost. The capital cost per kg H₂ capacity is \$160 for a LH₂ tanker and \$950 for a 550 kg, 250 bar compressed H₂ delivery truck [11]. Future pipelines may slightly reduce the cost of compressed H₂ delivery, but they require high capital investment and are unlikely to reach remote destinations.
- Dispensing LH₂ at the station is also less expensive. Compressed H₂ dispensing demands compressors, a storage cascade of high-pressure vessels, and possibly a refrigerator to avoid excessive vehicle vessel heating during fueling due to compression work [28], [29]. LH₂ dispensing, on the other hand, is accomplished with inexpensive and efficient LH₂ pumps, minimizing fueling station cost and electricity needs [11].

Paster et al. [11] have analyzed efficiency and cost of H₂ production and delivery, including liquefaction, compression, distribution, and dispensing, and the results indicate that all forms of hydrogen delivery (LH₂ tanker truck, CGH₂ tube trailer, and pipeline CGH₂) *cost essentially the same* (\$4.25-4.80/kg H₂), because inexpensive LH₂ delivery and dispensing compensate for the high cost of liquefaction.

Beyond the essentially equal cost of vehicle refueling, the superior density of LH₂ enables a key advantage: compact, high capacity LH₂ storage that enables practical driving range and costs less because it demands less material (composite and metal) for manufacture. Recent analysis [11] has concluded that cryogenic pressure vessels have the *minimum ownership cost* (fuel cost + storage system cost, \$/km) of all hydrogen storage technologies, even after including the cost of liquefaction.

Focusing now on energy, we consider that in the long term H₂ will most likely be produced from renewable or nuclear electricity by water electrolysis (~70% efficient). The total electricity to produce 1 kg H₂ will be $\sim 33.3/0.7 = 50$ kWh/kg. Total energy consumption is therefore ~53 kWh/kg for compressed H₂ and ~63 kWh/kg for LH₂ – a 19% premium for LH₂. LH₂'s favorable properties, however, mitigate the difference:

- Efficient distribution: A LH₂ truck transports 7 times more H₂ than a tube trailer, reducing truck fuel and delivery energy consumption.
- Lower vehicle weight: cryogenic vessels are lighter than compressed gas and sorbent vessels, resulting in lighter vehicles with higher fuel economy. Less H₂ is therefore necessary for the desired vehicle range, thereby reducing energy consumption.
- LH₂'s thermomechanical exergy: Defined as the maximum theoretical work that can be done when bringing a substance into pressure and temperature equilibrium with the environment, the thermomechanical exergy of LH₂ is rather large. At 3.47 kWh/kg (~10% of the lower heating value of H₂ without considering para-ortho conversion) the thermomechanical exergy can lengthen vehicle range by e.g., air conditioning the cabin, cooling down the fuel cell, supercharging the internal combustion engine, or producing power in a thermodynamic (e.g. Rankine) cycle.

While it is clear that these three effects can mitigate the LH₂ energy premium, it is unimportant for future hydrogen transportation whether the final energy balance favors LH₂ or compressed H₂. Instead, enabling safe, long range, cost effective, and practical vehicles is what ultimately matters. As described in this paper, all these advantages are in the side of cryogenic pressure vessels.

Vacuum Stability

Multilayer vacuum insulation consists of many layers of shiny metalized plastic located inside a vacuum. Vacuum reduces conduction and convection heat transfer, while metalized plastic reduces radiation heat transfer. This approach minimizes all forms of heat transfer and produces the highest performance thermal insulation available [30]. It is therefore the preferred technology for transportation applications where weight and volume are at a premium [2]. Multilayer vacuum insulation, however, demands a high quality vacuum. Typical vacuum insulation performance degrades when pressure increases beyond 0.01-0.1 Pa [30], [31]. At this point, enough gas molecules exist in the vacuum space to significantly contribute to heat exchange.

Unlike laboratory vacuum insulation systems that typically operate for short times and may be regenerated with a vacuum pump whenever necessary, automotive systems present a challenge because they require continuous operation for as long as 10 years with little or no maintenance. This level of vacuum stability frequently demands the use of metallic surfaces baked at high temperature to eliminate adsorbed species. Cryogenic pressure vessels have a non-metallic composite surface in contact with the vacuum (Figure 1) and may therefore present vacuum stability issues due to composites' tendency to outgas and the relatively low baking temperature (350 K) that composite vessels may withstand without risking structural damage.

Considering the importance of long-term vacuum stability on cryogenic pressure vessel insulation performance, we have conducted 11 experiments at varying LH₂ densities (13-62 g/L) over 20 months (May 2010-December 2011), with each individual experiment lasting 1-2 months. These experiments were conducted on a full-scale vessel (generation 2, Figure 6).

The experimental sequence starts with vacuum regeneration. Although desirable, oven baking proved impractical due to the large dimensions of the vessel. Instead, the vacuum jacket was wrapped in heating tape, which supplied enough power to heat up the vessel to 50°C. Heating continued for 3 days with the vacuum pump running. The vessel was then allowed to cool down to ambient temperature with the vacuum pump still running. The vacuum regeneration procedure was only performed three times during the whole experimental sequence: (1) at the beginning of the process, (2) after the August-September 2010 test, and (3) after the October 2010 test. This allowed us to observe “fresh” vacuum performance as well as accumulation of outgassing molecules in successive experiments, in an effort to predict long-term vacuum stability.

After reaching ambient temperature, the vacuum pump was disconnected and the vessel was cooled down to LH₂ temperature and filled to varying densities with saturated LH₂ at 1-2 bar and monitored during 1-2 months as the vessel heated up and pressurized due to environmental heat transfer. Vacuum pressure was also monitored during the experiments.

Experimental results (Figure 8) show that vacuum pressure follows a consistent shape as the vessel heats up due to environmental heat transfer. The experiments always start with a high quality vacuum (<0.001 Pa). The very cold vessel (initially at 21-25 K) can freeze outgassed molecules (except for H₂ and He, which not present in large concentration), and therefore acts as a very efficient vacuum pump. As the vessel warms up, molecules slowly evaporate and vacuum slowly pressurizes, reaching 0.01 Pa at ~50 K and 0.1 Pa at ~120 K. Vacuum pressure remains below 1 Pa up to 250-270 K – relatively high temperatures that may only be reached in vehicles that remain parked for a long time. Finally, vacuum pressure increases rapidly as the vessel approaches ambient temperature, reaching close to 100 Pa.

As previously discussed, the vacuum was not regenerated after every experiment. The effect of having a fresh vacuum vs. accumulating outgassed molecules from previous experiments is evident in Figure 8. Comparing the October 2010 test (black line) with the October-November 2010 and the December 2010 tests (blue lines), we can see that vacuum regeneration reduces pressure in the 120-170 K temperature range by about a factor of 2. Later tests (January-February 2011 and February-December 2011) show that vacuum pressure

gradually increases from test to test, and the February-December 2011 test is almost at the same pressure as the October 2010 test.

In summary, vacuum pressure is mainly a function of vessel temperature, but for any given temperature there is a clear effect of time elapsed since the last vacuum regeneration.

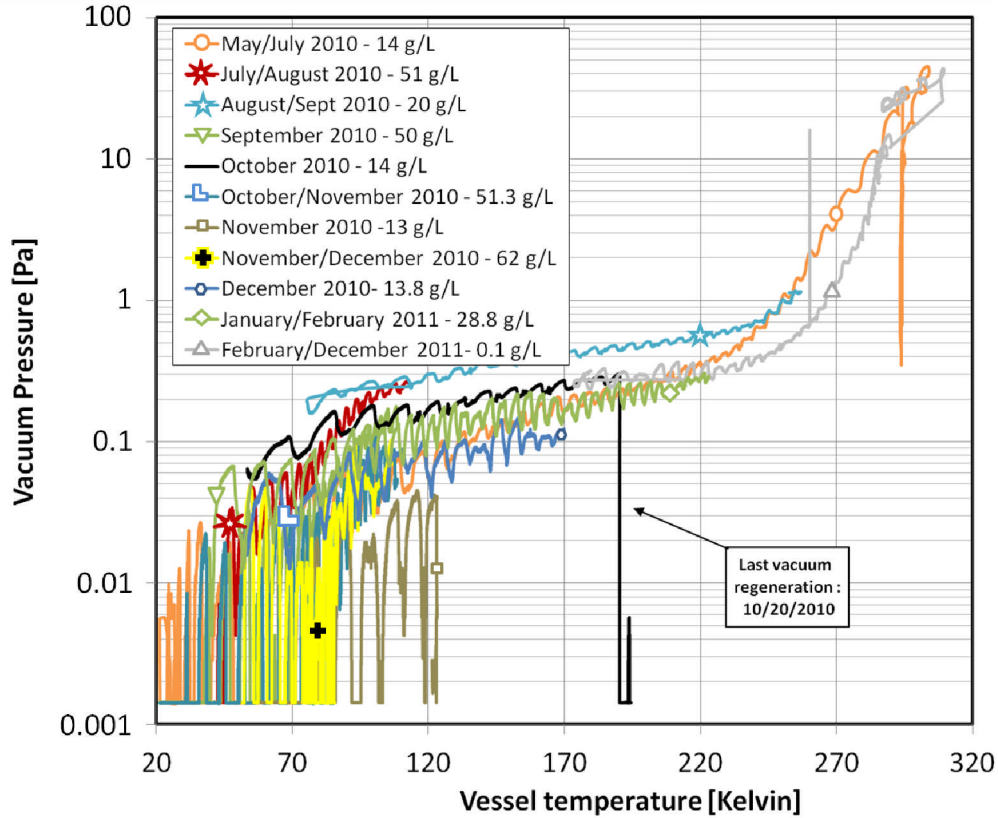


Figure 8. Pressure in the vacuum jacket as a function of vessel temperature. The figure shows results for 11 consecutive experiments spanning 20 months (May 2010-December 2011). H_2 density in each experiment is listed in the figure legend.

Figure 9 shows in more detail the results for the May-July 2010 experiment (14 g/L H_2 density). In addition to vacuum pressure, Figure 9 also shows heat transfer rate into the vessel, calculated from the first law of thermodynamics and including contributions from H_2 and vessel thermal mass as well as the energy absorbed by para-ortho H_2 conversion (Figure 4).

Cyclic variations in heat transfer and vacuum pressure in Figure 9 are due to day/night temperature oscillations (ambient temperature varied between 285 and 310 K during the test). Beyond the daily cycles, it can be observed that the daily *average* heat transfer rate (dotted line) is a non-monotonic function of temperature. This non-monotonic behavior can be explained as the competition between two factors that determine heat transfer: temperature difference ΔT between environment and vessel, and insulation performance, which is very sensitive to vacuum pressure. As the vessel warms up, ΔT decreases but insulation performance degrades due to increase in vacuum pressure.

From Figure 9, it can be observed that heat transfer rate remains fairly constant between 20 K and 120 K at 4.5-5 W. In this regime, the reduction in ΔT compensates for the lower vacuum quality, and both effects nearly cancel out. Between 120 and 170 K, the vacuum effect dominates and heat transfer is observed to increase to ~ 6 W. Further increases in temperature to 170-270 are not accompanied by large increases in vacuum pressure, and therefore heat transfer drops to its minimum (~ 4 W). Finally, the very rapid increase in vacuum pressure at near ambient temperature (270-300 K) produces a considerable increase in heat transfer (to 8 W daily average), even though ΔT is rather small in this regime (10-30 K). High vacuum pressure also increases the amplitude of daily heat transfer oscillations, because the lower effectiveness of the insulation exposes the hydrogen to the changing ambient temperature.

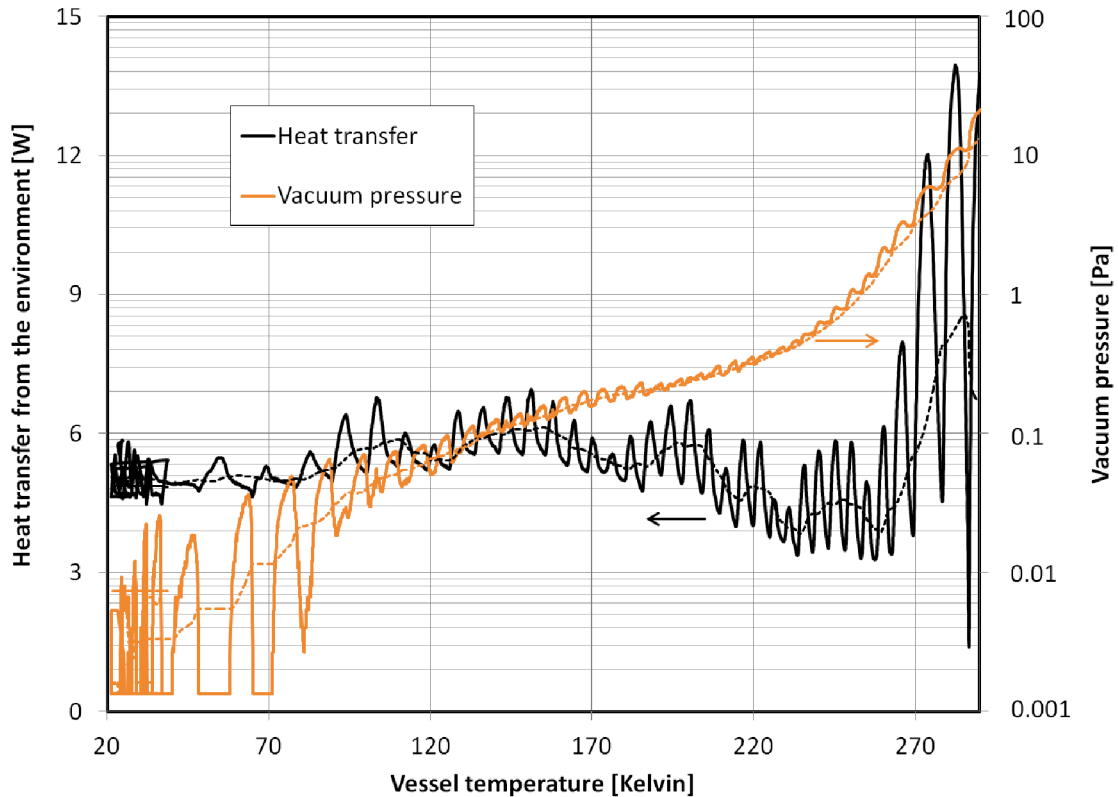


Figure 9. Vacuum pressure and heat transfer rate as a function of vessel temperature, for the May-July 2010 experiment. Solid lines show instantaneous values and dotted lines show daily averages.

Figure 9 indicates that heat transfer into the vessel is a relatively weak function of vacuum pressure. Average heat transfer only doubles from 20 K to 300 K, even though vacuum pressure increases by 4 orders of magnitude. This result may facilitate cryogenic vessel thermal control under regular use scenarios. Auto manufacturer BMW has recently analyzed thermal behavior of cryogenic pressure vessels as a function of use patterns, concluding that a vessel in a frequently driven vehicle (66 km/day) operates between 90 and 120 K (cooling during the refueling process). Vessels on commuter vehicles (44 km/day) operate at 110-160 K, and vessels on infrequently driven vehicles (22 km/day) reach equilibrium temperatures between 140-220 K [32]. From Figure 9, *all* these vessels would maintain a reasonable heat transfer performance

between 5 and 6 W.

While promising, these results are incomplete because automobiles operate for ~10 years with limited maintenance. It is therefore necessary to conduct vacuum stability tests over *years* to analyze long-term vacuum degradation. Getters contribute to vacuum stability, and they need to be carefully selected and designed for the task at hand. Future experiments are necessary for testing the vessel-getter system and evaluate long-term vacuum performance.

Conclusions

Cryogenic pressure vessels are composed of a high-pressure inner vessel made of carbon-fiber-coated metal (similar to those used for storage of compressed gas), a vacuum space filled with numerous sheets of highly reflective metalized plastic (for high-performance thermal insulation), and a metallic outer jacket. Cryogenic pressure vessels operate at low temperature (down to 20 K) and are designed for high pressure (350 bar). H₂ density at these conditions is considerably higher (~2x) than for compressed H₂. High density operation yields considerable advantages:

- *Maximum Range* for given volume and weight comparable vessels.
- *Only technology to meet DOE 2017 targets* for weight and volume.
- *Lowest ownership cost* due to compact vessel construction demanding smaller amount of expensive materials (composite and metal).
- *Improved Safety*: ~10x lower expansion energy for cold H₂ vs. ambient temperature H₂. Vacuum jacket provides secondary containment eliminating potential for environmental damage. Vacuum space provides expansion volume, mitigating expansion energy in case of vessel failure. Potential for less pressure cycles due to higher capacity.
- *Rapid, low loss refueling* with efficient and inexpensive cryogenic LH₂ pumping.

This paper presents a summary of cryogenic pressure vessel technology. Several technical issues have been identified, and some of their technical solutions have been found or proposed:

1. Evaporative losses in cryogenic vessels are essentially eliminated due to high-pressure capability. Hydrogen is contained even as it warms up and pressurizes. When H₂ is extracted during driving, the vessel cools down due to isentropic expansion.
2. Pressure vessels manufactured for storing compressed gas at ambient temperature have demonstrated to work well at cryogenic temperature. Further experiments will be conducted to guarantee safe operation at low temperature.
3. Cryogenic pressure vessel refueling can be accomplished rapidly (~5 minutes), at high density (~80 g/L), and with low evaporative losses with a commercially available LH₂ pump.
4. H₂ liquefaction is frequently considered too energetically intensive for practical transportation. Recent analysis [11], however, has demonstrated that the high cost of delivering, compressing, and storing compressed H₂ compensates for the high cost of liquefaction, and the *total* cost of dispensed hydrogen is essentially equal for liquid and compressed gas.

Vacuum stability, necessary for long-term (~10 years) cryogenic pressure vessel thermal insulation performance, is the key outstanding technical challenge. Preliminary analysis shows that if the cryogenic pressure vessel operates below 250 K, vacuum degradation would have a somewhat low impact on the performances of the system. Vacuum recovery by thermal cool down is under investigation. Finally, vacuum stability could be improved using high temperature baking and custom getters as possible technical solutions.

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